

Inorganic Chemical Technology
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Lecture - 31
Raw Materials and Basic Ceramic Chemistry

Welcome to the MOOCs course Inorganic Chemical Technology. The title of today's lecture is Raw Materials and Basic Ceramic Chemistry.

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Ceramic industry

- Traditional name of ceramic industries is “clay products” or “silicate industries”
- Variety of products of ceramic industries are essentially silicates only
- Pottery and burnt clayware have been found since ancient days → pottery clayware
- Demand for superior materials have led to broader spectrum of products
- To meet such demands, modern methods of fabrication inventions led to cross-fertilization of silicate chemistry with metallurgy and solid-state physics
- Modern fabrication methods also aided by coupling with many computer controlled processes and advancing automation
- New processes have been developed for brickmaking from inorganic wastes such as
 - Fly ash from power plants
 - Foundry sand
 - Mine tailings
 - Furnace slag and a large variety of other materials

*China
Bl
ceramic
slab*

In this particular week, we are going to discuss about ceramic industry. Most of the products of ceramic industries are some kind of clayware or potteries, etcetera, right. So, because of that reason, traditional name of ceramic industries is also clay products, right. Not only clay products, it is also known as silicate industries because most of the clays are having one or other kind of silicates, right.

So, that is, variety of products of ceramic industries are essentially silicates only. Because of that reason the ceramic industry was known as a silicate industries in earlier days, traditionally, ok. However, nowadays so many varieties of products have been developed based on the consumer needs, etcetera. So, because of that one, calling ceramic industry, silicate industry in today's context is not appropriate.

Because there are some kind of ceramic products which are produced with some basic knowledge or basic information input, not only from the knowledge point of view, but also from the material point of view. Some inputs are there from the metallurgical industry as well. So, calling them only silicate industry is not appropriate in the present day context, ok.

Some of the ancient days examples of ceramic industry products are pottery and then burnt clayware, etcetera. But nowadays, demand for superior materials have led to broader spectrum of products. Earlier, you have only some kind of potteries or claywares only were you know being produced in ceramic industries.

But nowadays, what happens? So many demands have come for different types of products. Like, you know some kind of semiconductor chips also, they are also it is required to have a you know specified design and then product requirement which are produced not only from the products, not only from the raw materials of the ceramic industry, but also from metallurgical industry also.

For example, like many people in place of their broken teeth, they used to have a silver crown or gold crown teeth etcetera, they may be implanted, right. So, there you know kind of a cross fertilization of a ceramic industry with metallurgical industry is done. Similarly, for several semiconductor chips also some kind of combination of a ceramic industry knowledge and in metallurgy knowledge is required, ok.

So, because of such kind of demand for superior materials or different types of material, the spectrum of products of ceramic industries has become very broader these days. So, when you have a broader spectrum of products, then obviously, you need to have a you know much more input to get such kind of products.

So, in order to meet such demands, modern methods of fabrication inventions have led to cross fertilization of a silicate industry with metallurgy and solid state physics, ok. Modern fabrication methods also aided by coupling with many computer controlled processes and advancing automations.

Because sometimes when you prepare such kind of semiconductor chips, etcetera and then gold crowned teeth, etcetera, you know you need to control the process conditions very specifically of required temperature within plus or minus 5 degree centigrade.

Especially, when the operating temperature is very high in the range of 900 or more than 900 or 1000 degree centigrade, etcetera.

You know controlling temperature within small range of error of plus or minus 5 percent degree centigrade is very difficult when the range of operating temperature is very high like you know 1000 degree centigrades, 1200 degree centigrade, something like that. So, for that it is very essential to have computer controlled processes and then advancing automation technology, you know are very much essential for the growth of the industry.

Not only from you know basic raw materials of ceramic industry, and then, with some inputs from the metallurgical industry variety of ceramic products are produced, but also, from waste also different types of ceramic products are in general developed. Something like you know some inorganic waste, like fly ash from the power plants.

You know that may be fly ash usually you know mostly is a waste product, it is not being utilized for any other purpose. So, that is being utilized by the ceramic industry to make different types of you know bricks. Similarly, mine tailings, etcetera they are also a kind of wastage product from the prospective of the mine industries, right. So, those mine tailings also utilized to get or prepare some kind of bricks or ceramic products.

Likewise, you know metal slags in metallurgical industries after getting the refined product of required nature, required characteristics a lot amount of metal slag is produced. There may be important ingredients in those metal slags, but recovering them may not be economically feasible, right. So, because of that reason, it is better to utilize them for some other application. So, such kind of metal slags are also used for a brick making kind of thing which can be done by ceramic industry principles.

So, thus, as explained, several types of bricks can be made from different types of inorganic waste. And then, what are the such inorganic waste which can be utilized for making bricks? Fly ash from power plants, foundry sand, mine tailings and then furnace slag and a large variety of other materials as well.

Now, from the product point of view, if you wish to have a product from a ceramic industry what kind of characteristics you supposed to expect or you may be expecting in general. So, especially you know from the applications point of view, either in plant applications or in household applications or societal applications etcetera, you first see

like that material must be mechanically stable, that must be chemically stable, that must be thermally stable, such kind of characteristics you see. So, those characteristics we are seeing now.

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The slide contains a list of characteristics for ceramic materials:

- New products from ceramic industry have been developed as per the demand for materials that are
- Thermally stable: withstand higher temperatures
- Mechanically stable: resist greater pressure and superior mechanical properties
- Chemically stable: protect against corrosive chemicals
- Possess special electrical characteristics

Handwritten notes on the slide include:

- A red circle around the text "Glass making ceramic materials".
- A diagram showing "electric" leading to "Storage device" and "Energy filter".
- A red circle around "Furnaces".
- A red circle around "1200-1400°C".
- Arrows pointing from "Furnaces" to "1200-1400°C".

New products from ceramic industry have been developed as per demand for materials. Those materials should have following characteristics. Thermally stable, materials we can say thermally stable if they can withstand higher temperatures, higher temperatures of several 100 degree centigrades or even sometimes more than 1000 degree centigrades also.

Let us say furnaces, right from the chemical industry point of view or application in industry point of view, these furnaces are made up of several types of refractories, right. So, we have seen some of the refractories are used for making glass making etcetera in one of the previous week lectures, right.

So, now what we have seen? So, the operating temperature in those furnaces is very high, order of 1200 to 1400 degree centigrade something like that, right. So, the raw materials are fed into the furnace, and then furnace is supplied energy, so that to raise the temperature to you know require temperature of 1000 1200 or 1400 degree centigrade something like that. So, at this temperature definitely there would be reactions amongst the materials that have been fed to the furnace, right.

So, now the refractories that are being used to make this furnace they should be chemically stable as well as the thermally stable. Thermally, they should be stable up to this temperature or even beyond that one and then what are the products are forming chemical products are forming; what are the input chemical reactants given to those furnaces at such high temperature.

So, these refractories should be chemically stable to those chemical nature of the components as well. So, that is also required. So, this is from the chemical industry point of view, right. If you have a sewage, you know sludge etcetera, they are allowed to flow through certain kind of enclosed area where you need sewage tiles etcetera. So, these sludges etcetera are very acidic actually in general. Though the temperature may not be very high in such conditions, but they are very acidic, right.

So, then you know when the material or sludge passes through such enclosed area which is you know covered with sewage tiles etcetera. So, then the sewage tiles should be you know chemically stable against those kind of those acidic sludges etcetera. So, chemical stability is also required.

So, like that if you keep on saying that mechanical stability is also a very much essential, right. You know floor tiles etcetera you in general have, and then, you know sometimes you know what happens at the household purpose or office hold purpose also you may be shifting or moving the furniture from one place to the other place and then weight of such furnitures may be very high in general some 100s of Kgs or something like that.

So, if these tiles floor tiles etcetera are breaking to such mechanical weight itself, so then that is not going to good. So, that is the reason you know you need to have a mechanical stability in your product, ok. So, the second one is mechanical stability. So, that product should resist greater pressure and superior mechanical properties.

Then, chemically stable, they should protect against corrosive chemicals, right. Sometimes you know your product your ceramic product should have all these 3 characteristics as per requirements. Let us say furnaces made up of refractories etcetera one good example, right.

Such kind of examples we have already seen in other classes where you know glass making and then cement industries etcetera, in those cases we have seen you know so

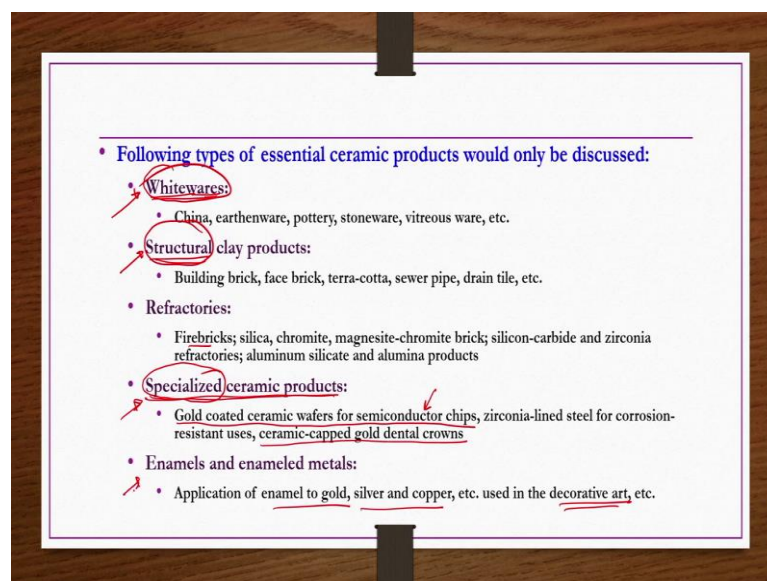
much of you know these materials which are used for this ceramic making you know they are also there. So, you expect to have all these thermal stability, mechanical stability and chemical stability in one single applications.

In sometimes in for given applications, you may look at only one particular important characteristic like you know thermal stability, other applications you primarily concentrate on mechanical stability, other applications you may concentrate on chemical stability.

But sometimes you know there may be cases, in some applications, you may require to have a stability against thermal applied temperature, mechanical forces and in chemical corrosiveness etcetera all of them together. Also, possess special electrical characteristics as well, ok. So, those are the requirement of a ceramic products. You supposed to expect or you are expected to make a ceramic product which is thermally mechanically and chemically also stable, right.

So, now what could be such kind of products in general? Right. So, if you see you know range of ceramic industry products is now broader. It is no more very limited in general. So, however, we try to have a classification of a different types of a ceramic industry products and then see what are they. And then, we will be discussing about those kind of ceramic industries products only in this and in coming lectures.

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Following types of essential ceramic products would only be discussed because of time limitations, ok. Whitewares is one type. Another one is the structural clay products. Another one is the refractories. 4th one is specialized ceramic products, and then finally, enamels and then enameled metals.

These 5 types of ceramic products we are going to discuss in detail from their manufacturing applications, and then, uses etcetera point of view, we are going to discuss this 5 types of ceramic products. Now, what are the things that are covered under the whitewares or what are the ceramic products that comes under a whitewares? They are nothing but Chinaware, earthenware, pottery, stoneware, vitreous ware etcetera.

By name whiteware, why the name is given whitewares for them because mostly their appearance is white in color. There may be some kind of textures and then some designs may also be there of different colors, but primarily these products you know they are in white in color. So, that is the reason they are known as whitewares.

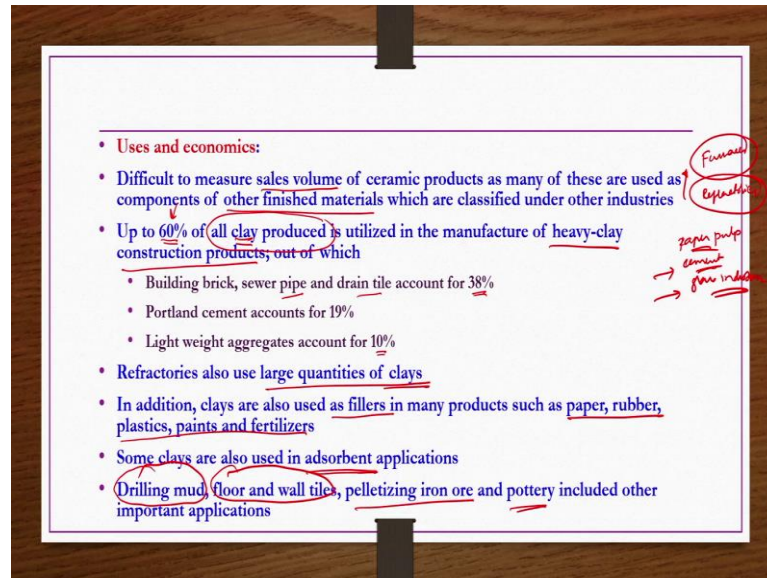
Similarly, second one is the structural clay product. Structural clay products the name by the structural means the products that are produced by ceramic industry, they are used to make some kind of structures, like you know some kind of bricks etcetera. So, those things comes under structural clay products category that is building brick, face brick, terracotta, sewer pipe, drain tiles etcetera.

Next one is the refractories which include fire bricks, silica brick, chromite brick, magnesite, chromite brick, silicon, carbide brick, zirconia refractories and then silicate, aluminum silicate, alumina products etcetera all comes under the refractories. For the case of specialized ceramic products, like gold coated ceramic wafers for semiconductor chips are one of the common application for the specialized ceramic products or it is one of the important product that comes under specialized ceramic products.

Similarly, ceramic capped gold dental crowns and then zirconia lined steel for corrosion resistant uses etcetera, all they come under specialized ceramic products. Specialized because they are developed for the specialized applications like you know semiconductor chips or you know gold dental crowns etcetera for those purpose special application purpose they develop. So, that is the reason these products are you know called as specialized ceramic products.

Likewise, under enamels and enamel metals applications of enamel to gold, silver and copper etcetera used in different types of decorative art etcetera those kind of products comes under this category.

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Now, we discuss about uses and applications and economics of a ceramic industry. In ceramic industry it is very difficult to measure the sales volume of ceramic products because many of these are used as components of other finished materials which are classified under other industries.

Let us say furnaces one example, furnaces or manufacturing or development of furnaces does not come under ceramic industries. But you know whatever the refractories are used for making such kind of furnaces, they are produced by the ceramic industry. But you know they are utilized for some other industry that is the reason such kind of many cases are there. You know the products are primarily of ceramic industry, but from the end use wise they are in some other industries or for some other purpose.

So, that is the reason getting or measuring the appropriate sales volume of ceramic products is very difficult, ok. Up to 60 percent of all clay produced, clay not the product, clay produced utilized in the manufacture of heavy clay construction products and then out of this 60 percent of clay that is used for a heavy clay construction products you know out of which building brick, sewer pipe and then drain tiles account for 38 percent,

19 percent account for Portland cement, light weight aggregates account for 10 percent, right.

And more examples under these cases of products of ceramic industries or you know ingredients of ceramic industries are used in some other industry or like you know they include paper and pulp industry, cement industry, glass industry. You know so many things associated with the ceramic industries, they are also associated with the cement and glass industry. And the same you can realize as we progress ahead into the course of a ceramic industries.

Refractories also use large quantities of clays. Clays are also used as fillers in many products such as paper, rubber, plastics, paints and fertilizers. Some clays are also used in adsorbent applications like silica etcetera, they are also used as adsorbent. And then silica is one of the important component of a ceramic industry. Other applications include drilling mud, floor and wall tiles, pelletizing iron ore, pottery etcetera all they may be included in the uses and applications of ceramic industries.

Now, we have seen a few basics of a ceramic industries and then what are the different types of characteristics that you expect from a given ceramic product and then what are the different types of ceramic products are possible etcetera; applications, uses etcetera those things we have seen. Now, we see basic raw materials of the ceramic industry. This particular lecture is targeted primarily on basic raw materials and then basic ceramic chemistry.

So, first part of the lecture we are going to start now. That is on basic raw material. Why are we discussing so much about the raw materials? Because that we are going to realize in almost all ceramic products, clay is one of the important raw material. Then, along with that one there are other raw materials like you know sand, feldspar etcetera are there, that is the reason it is very much essential to understand or learn a few basics about such raw materials as well, ok.

Rather simply mentioning these are the raw materials utilized for production of several ceramic products, it is important to understand their basic chemistry as well.

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• **Basic raw materials:** Three main raw materials are

- Clay
- Feldspar
- Sand

• **Primary source of feldspar mineral is igneous rocks**

• **Clays are more or less impure hydrated aluminum silicates resulted from weathering of such rocks as per reaction:**

• $K_2O \cdot Al_2O_3 \cdot 6SiO_2$ (Potash feldspar) + CO_2 + 2 H_2O
 $\rightarrow K_2CO_3$ + $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ (Kaolinite) + 4 SiO_2

• **Discussing individually about these raw materials is essential**

So, basic raw materials of ceramic industry, 3 main raw materials are very common in any of the ceramic product that you take. So, one of them is clay, another one is the feldspar, third one is the sand, ok. Primary source of a feldspar mineral is igneous rocks. Clays are more or less impure hydrated aluminum silicates resulted from weathering of such rocks as per the reaction given below.

That is if you take potash feldspar actually, feldspar different types of feldspar are there, potash feldspar and then soda feldspar, lime feldspar etcetera that based on the feldspar you know Al_2O_3, SiO_2 are common and then third one whatever is there based on that one the name is given.

Now, here K_2O is there, so that is the reason this feldspar is having the name of potash, feldspar. If it reacts with carbon dioxide and water at high temperatures then you get a clay mineral, one of the clay mineral is kaolinite which is having the formula $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, right. This is one of the material from or one of the clay mineral that is required for almost all ceramic products production, ok.

So, when this reaction takes place along with the potassium carbonate and then silica you get a clay mineral kaolinite which is very essential for most of the ceramic products manufacturing. So, now what we do? We discuss individually about each of them.

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• **Clays:**

- No. of mineral species are available, known as clay minerals
- These mainly contain mixtures of
 - * **Kaolinite** ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$)
 - **Montmorillonite** [$(\text{Mg}, \text{Ca})\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2 \cdot n\text{H}_2\text{O}$]
 - **Illite** (contains variable amounts of K_2O , MgO , Al_2O_3 , SiO_2 , H_2O)
- From ceramic industry viewpoint, clays are **plastic and moldable** when sufficiently finely pulverized and wet, rigid when dry, and **vitreous** when fired at a suitably high temperature
- Most importantly, manufacturing processes depend upon these properties of **clay**

Now, we talk about clays. Clays are primarily having several types of minerals. They are also known as the clay minerals. These minerals include several types of inorganic oxides, primarily inorganic oxides should be there. Some of them may be important for a given application of ceramic industry. Some of them are important for a given application of glass industry, some of them are may be important for the given application of cement industry like that are there.

So, what we have to do? We have to do a kind of a clay upgrading, so that to get the required minerals which are essential from the ceramic products making point of view, ok. So, number of mineral species are available which are known as clay minerals. These mainly contain mixtures of kaolinite which is having formula $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$.

Then, Montmorillonite which is nothing but $\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2 \cdot n\text{H}_2\text{O}$ or $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2 \cdot n\text{H}_2\text{O}$ right. Then, third one is illite which contains variable amounts of K_2O , MgO , Al_2O_3 , SiO_2 , H_2O . Now, you see you know all of them are inorganic oxides except this H_2O component because H_2O is coming because these are hydrated, right.

So, you see primarily inorganic oxides only. So, clay is primarily consisting of inorganic oxides. So, out of which this kaolinite is used to larger extent to produce different types of inorganic, different types of ceramic products. From ceramic industry viewpoint, clays are plastic and moldable. You know, they should be moldable actually. This clays

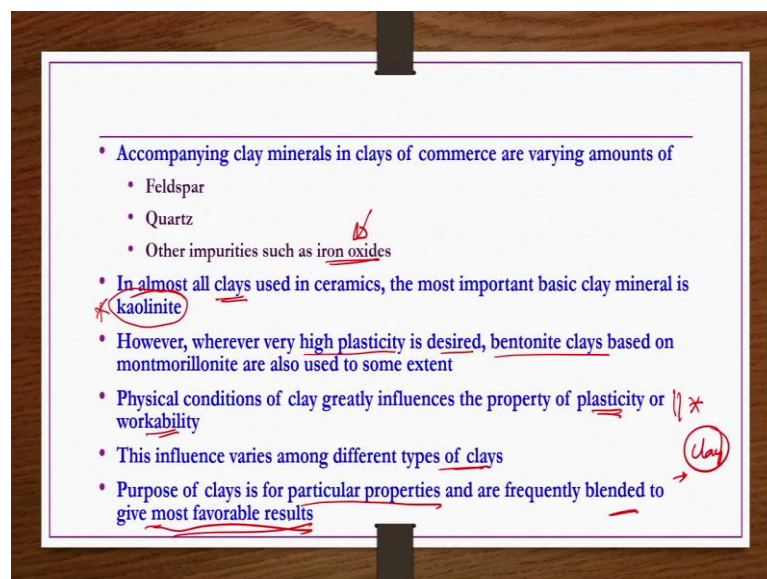
etcetera, feldspar etcetera and then sand etcetera, you take together and then you heat it to the higher temperature, so certain reactions taking place, right.

So, those things we are going to see anyway. So, when such reactions takes place, you get a you know liquefied sample which should be in a moldable conditions, right, so that you can make a required product shape and then you know design etcetera. So, clays should be plastic and they should be moldable when sufficiently high temperature is supplied to those clays, then only it is a good one for production of certain kind of ceramic products, ok.

So, these clays should be finely pulverized and then wet, they should be wettable because without if they are not wettable, it is going to be very difficult to make a product of required shape, right. And then when they dry, they should be rigid. And then when you fire them at high temperature or calcine them at high temperature like 1200, 1400 degrees centigrade, they should be vitreous, ok.

So, from the ceramic industry viewpoint, clays should be plastic and moldable when sufficiently finely pulverized and wet, rigid when dry, and vitreous when fired at suitably high temperature. Most importantly manufacturing process depend upon these properties of clays. So, all these properties, we are going to discuss from the product point of view.

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So, now what are these clay minerals in general include? They include varying amounts of feldspar, quartz and then other impurities such as iron oxides, ok. So, obviously, when you have impurities, you know they should be removed. They may not be impurities for other industry like metallurgical industry or something like that, but they are impurities as far as we are concerned about the ceramic industries.

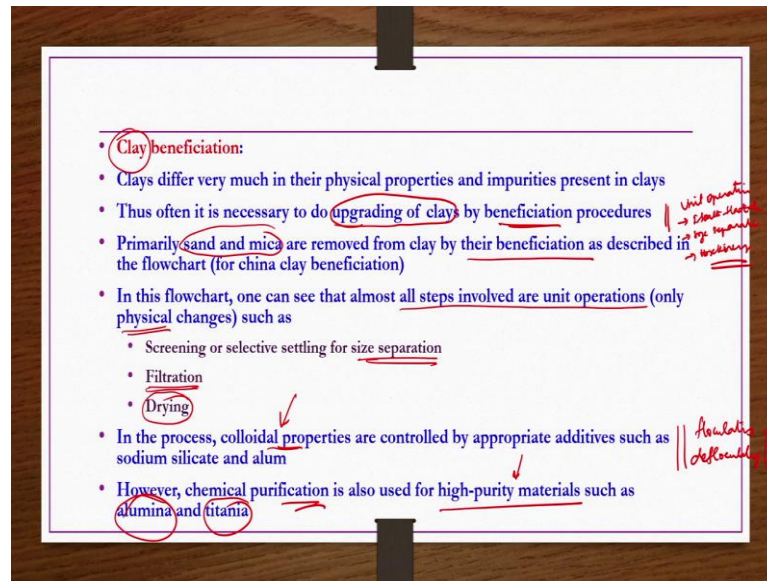
So, now from the ceramic industry's point of view, such impurities should be removed. Other kind of impurities may include like mica etcetera, they should be removed. In almost all clays used in ceramics, the most important basic clay mineral is kaolinite. This is very much essential, ok.

However, very high plasticity is desired, bentonite clays based on montmorillonite are used to some extent. What do you mean by actually high plasticity and then high workability or moldability? When you apply high temperature to the raw materials mixture, they become liquid kind of products and then they should have proper flowability etcetera. So, then we can say that the material is having in a workable kind of conditions, ok.

Physical conditions of clay greatly influence the property of plasticity or workability definitely. And then, the influence varies among different types of clays. One clays to other clays, the whatever the influence of this clays is there, so that is going to be changing. Purpose of clays is for particular properties and are frequently blended to give most favorable results.

Different clays are used actually, though we are calling like kaolinite is one of the mostly used clay in ceramic industry, but other types of clays are also there, right. So, they are also used. You know each one is having certain kind of you know applications, certain kind of characteristics. But it has been found that when you mix them frequently, you know blend them, so then you get most favorable results from the product point of view.

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So, as we have already seen, the clays that are we are having, you know it is having impurities, impurities like sand, mica, iron oxide, etcetera. So, they have to be removed. Removal of these impurities from the clay is known as clay beneficiation. We are not calling clay purification because clay is not one single component that we are purifying. It is a combination of different components, right.

So, but however, from this mixture of different components, we are removing some of the impurities. They are impurities from the ceramic industry point of view only, right. Otherwise, those impurities after removal, they can also be used in some other applications. Let us say iron oxide, if you are producing in a good quantity, so you can use it in metallurgical industry. Let us say mica, impurity you are separating in a large quantities, so that should be sent to the mica plant for a proper utilization point of view.

They are impurities from the ceramic industry point of view only. Clays differ very much in their physical properties and impurities present in clays. Thus, often it is necessary to do upgrading of clays. Upgrading in the sense, removing unnecessary or undesired components from the clays, ok.

So, this upgrading is done by beneficiation process, which is primarily you know includes unit operations only, unit operations. Whenever we have beneficiation, etcetera, you can clearly understand that you know there is a froth flotation possible. There is a

size separation is possible. You know thickening is possible. So, all of these things are unit operations only.

So, what you understand? You know not only this clay beneficiation, upcoming sections of production of different types of clay products, you see primarily you know unit operations are only involved, ok. Primarily sand and mica are removed from clay by their beneficiation. China clay beneficiation, flowchart we are going to discuss in the next slide anyway.

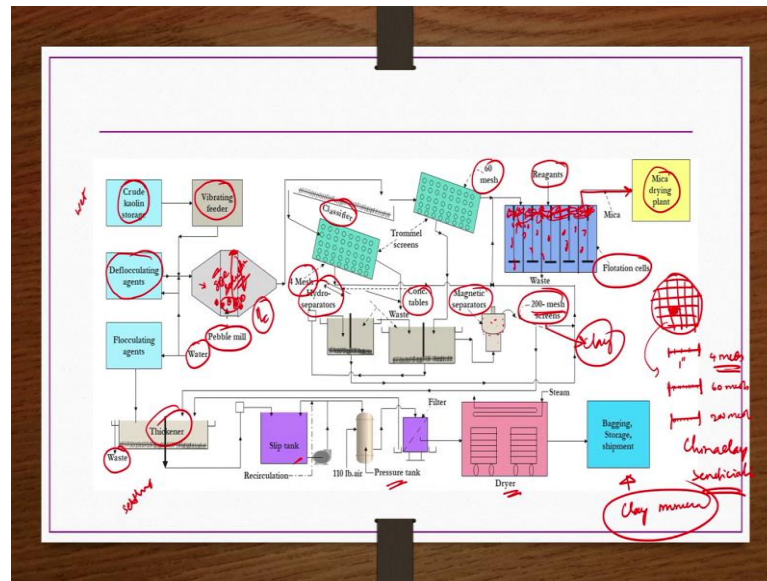
Here one can see that almost all steps involved in the China clay beneficiation are unit operations only. There are no chemical reactions. There are only physical changes are there, ok. Physical changes, size separation is one thing that you can definitely expect in separations of or you know, beneficiation of ore, etcetera, And that is done by the screening or selective settling for the size separation.

And then filtration would be there to filter out the unnecessary things, ok. Then, after filtration, you definitely need to dry the material before processing to the next level, ok. And there may be other kind of unit operations like, you know, thickener, etcetera hydrostatic separators or magnetic separators, etcetera those things may also be possible. So, we have listed only a few.

In this process, colloidal properties are controlled by appropriate additives such as sodium silicate and alum. You need to have a flocculating agents, etcetera. You need to have a de-flocculating agents, etcetera in the process. So, they are required to maintain the colloidal properties, ok. So, those things we are going to see.

However, chemical purification is also used for high purity materials such as like you need to produce pure alumina or pure titania, then you can go for a chemical purification, ok. But majorly, most of the clay products, you know, you do not need to go for a chemical purification of a clays. You can go for a clay beneficiation which is done by several physical steps or unit operation steps.

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Now, here we see the flow chart for the China clay beneficiation, right. Here, what we have? We have a pebble mill, right. To this one, we are feeding crude kaolin from the crude kaolin storage through a vibrating feeder. Why vibrating feeder? Because these may be having of different sizes, right. And then, may not be able to pass easily through the columns or you know pipes, etcetera. So, then a vibrator is provided to the feeder, so that, you know, vibration will enhance the movement of this particulate matter.

Usually, particulate matter does not flow down easily, even if it is by the gravity or by pressure or whatever. So, you know, storage and transport of solids is very difficult task. So, for that reason, you know, vibrating feeders are often used to transport the solid materials. So, this crude kaolin is fed to the pebble mill through a vibrating feeder.

To this one, you are also giving de-flocculating agents because these crude kaolin storage, whatever is there, from that, the material that you take that may be wet or bit damp. If it is wet or damp. So, it may not flow through easily. So, for that reason also, you need to have the vibrating feeder.

If it is wet or damp, then what happens? You know, when the material is taken to the pebble mill, where required size reduction is taking place. That will also not be efficient if the material is wet because if it is wet, you know, they may form lumps kind of thing. So, when it is forming lumps, so rather size reduction taking place, breaking of lumps

will only be taking place or most of the energy utilized for the size reduction would be utilized for the lumps breaking, which is not at all required.

So, for that reason, there are some de-flocculating agents are you know provided. So, these de-flocculating agents along with the water are provided here, ok. So, this pebble mill is nothing, but a cylindrical container, which will be rotating. And then rotational speed should be such a way that, it should not be more than the critical speed.

Critical speed is the one you knows at which the centrifugal forces are balanced by the gravity force. So, your rotational speed has to be less than the speed at which centrifugal force is balanced by the gravity force acting on the material that has been fed to this rotating drum, right. This pebble mill is nothing, but rotating drum way. You can visualize as a rotating drum.

To this drum, you have taken pebble. If it is a ball mill, you will be taking a balls, steel balls or you know wooden balls, etcetera. If it is a rod mill, so then you may be having metallic rods or wooden rods, etcetera may be there as a kind of you know grinding medium.

Now, here it is a pebble mill, so then pebbles of different sizes of different nature would be taken into the material as a grinding medium. To this one, when the material, whatever the kaolin is there that comes in, right. So, and then when it rotates, moment the rotation takes place the material, whichever was there at the bottom, that will be gradually moves up. And then, moment it reaches the top location, the material will fall down.

Now, the material is the combination of the feed material plus these pebbles. So, when they fall down. So, a kind of impaction takes place and then some grinding takes place and then material, size reduction takes place, right. So, size reduced material will then be passed through different steps of a unit operations like a classification, hydro-separation, and then concentration tables and magnetic separators, etcetera as per the requirement, right.

So, the magnetic separators are usually to catch the materials which are having magnetic properties, right. When this size reduced material comes and interact with these magnetic

separators, in the materials, if the material which is having magnetic properties, they will be captured here and then remaining material will be sent forward, right.

So, here, you know, mesh sizes or different mesh sizes are there as per the requirement, you know, the size operation is taken place. If you required 60 mesh size, so accordingly, the process would be taken place. If you need 200 mesh size materials, then accordingly these steps would be considered.

What do you mean by mesh size? I already explained. Let us say within a, if you have a sieve like this. So, within this screen or mesh, you take a one linear inch, one linear inch distance and then within that linear inch distance, let us say this is one linear inch distance, within this one, if you have only 4 openings, 1, 2, 3, 4. So, then this is called 4 mesh.

So, what you see? If the mesh number is smaller, the opening would be bigger. Let us say if you have a same one linear inch distance here from this screen you have taken, let us say if you have 60 openings here like this, then this mesh is known as 60 mesh. And then obviously, the opening should be smaller than the 4 mesh. So, 200 mesh, even smaller would be there like, you know, a few micron size opening would be there, ok. So, that is what the mesh anyway.

So, now after passing these materials, whatever the material that is coming over from the 60 mesh that is taken to a flotation cell to which reagents or flotation or froth forming reagents are supplied and then mechanical agitation is also done. So, that, you know, froth formation takes place and bubbles forms. Bubbles forms and the froth of bubbles, you know, rise to the top of the flotation cell, right.

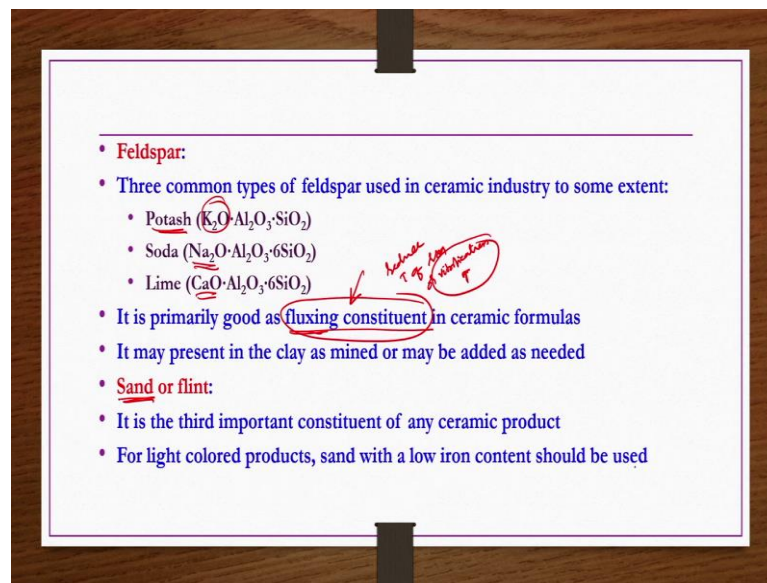
So, when they rise here, so whatever the material having the lower density that material will be stick to these bubbles and then they will be floating. So, in this case, mica is the one which is having lower density, so that will be attached to the bubbles and then they will be floating on the top. So, then they will be separated out and taken to the mica drying plant, ok.

Whereas, the material which is passed through 200 mesh, which is primarily having the desired clay minerals, you know, they will be taken to a thickener here. Here in the thickener are nothing but, you know, settling, you know, settling by the gravity. So, if it

is settling by the gravity, so then gravity thickener or if it is settling by the centrifugal force, then it is known as the centrifugal thickener, ok.

So, here the wastage material will be floating from the top that is taken and then from the bottom, which is the important clay mineral that will be followed through different sections of pressure filter and then dryer, etcetera to get the final clay mineral which has been purified, beneficiated using physical process, physical changes. There are no chemical reactions at all in this process, ok. That is about the clay beneficiation.

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Now, we go to the second raw material that is feldspar. 3 common types of feldspar used in ceramic industry to some extent. They are nothing but potash, soda and then lime based feldspar. So, potash based is nothing but K_2O , Al_2O_3 because of K_2O presence, it is known as a potash feldspar. Whereas, the soda is having Na_2O , that is the reason it is called as soda feldspar.

And then the next one is having CaO , that is the reason it is known as lime based feldspar, ok. It is primarily good as fluxing constituent in the ceramic formulas. What do you mean by fluxing? You know, they reduce, these components reduce the temperature of reaction or vitrification temperature. You need to do some kind of vitrification. Now, most of the ceramic products, if you see a kind of glassy shining kind of appearance you have, that is because of the vitrification, right.

So, that the vitrification is usually can be done at high temperatures for most of the ceramic products. But if you have a good fluxing constituents, the temperature would be reduced, right. That is the reason these components, they are some of these components are known as the fluxing constituents in ceramic product formulas, ok. It may present in the clay as mined or may be added as needed.

Third important raw material is sand or flint. For light colored products, sand with low iron content should be used.

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• Formulas and properties of basic raw materials for ceramics industry:

	Kaolinite	Feldspar	Sand or flint
Formula	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$	$\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$	SiO_2
Plasticity	Plastic	Nonplastic	Nonplastic
Fusibility	Refractory (infusible at highest T of coal fire, 1400°C)	Easily fusible binder	Refractory (infusible at highest T of coal fire, 1400°C)
Melting point (°C)	1785	1150	1710
Shrinkage on burning	Much shrinkage	Fuses	No shrinkage

Now, we see formulas and properties of basic raw materials for ceramic industry. So, from the clay minerals, we take kaolinite, from the feldspar we take a potash feldspar and then sand is the other one we are taking. Formula, plasticity, fusibility, melting point and shrinkage and burning are discussed here, right.

So, kaolinite formula we already know that $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$. It is plastic in nature, so it is a good one because most of these ceramic materials or you know raw materials of this ceramic industry, they should be plastic. And then fusibility, they are of refractive nature because they are not feasible even at temperature of 1400 degree centigrades. Why they are not feasible even at this temperature? Because their melting point is 1785 degree centigrade, right.

But the problem is that on burning, they undergo much shrinkage. From the thermal stability point of view, if you think that you know melting point is very high and then it is infeasible even at 1400 degree centigrade. If you think that you take most of the raw material as kaolinite, let us say 80 percent you take kaolinite and remaining 20 percent feldspar or sand if you take, you know you may not get a finer product.

You may have a thermally stable product, but you may not have a proper product because on heating, you know kaolinite undergoes much shrinkage which is not good, ok. So, feldspar, formula is $K_2O \cdot Al_2O_3 \cdot 6SiO_2$. It is a non-plastic, but it is easily fusible. Why it is easily fusible? Because its melting point is 1150 degrees centigrade only, right. So, but it fuses does not mean that it is not good.

When it fuses, what it does? It acts as a binder, it acts as a binder and then keep the components tight together themselves, right. So, it is not the feasibility that you have to see, but also other parameters also you have to see. And then on heating it fuses rather shrinking, ok.

Third one is the sand which is SiO_2 . It is a non-plastic and it is a refractory because its melting temperature is 1710 degree centigrade and because of that one it is infeasible even at 1400 degree centigrade. But good thing is that it does not go any kind of shrinkage on burning.

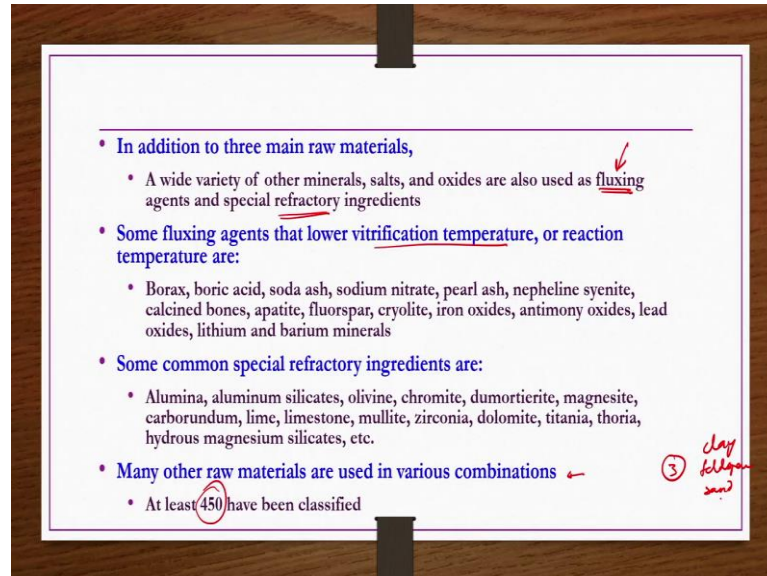
So, now you see one of the material is very much shrinkage, another one is the no shrinkage, another third one is the undergoes fusing on burning. So, important raw materials, 3 important materials are having 3 important characteristics. So, proper combination of these materials one has to take as per the requirement of the product and then make a required ceramic product.

So, because of their distinctive characteristics, all of them are very much essential from the ceramic products viewpoint. So, that is what we have seen about raw materials. Primarily, 3 important raw materials, clays, feldspar and then sand. So, we have discussed in detail about them and then we compare properties as well, right.

What does it mean by? Does it mean that ceramic industry is having only these 3 raw materials? No, there are n number of other raw materials are also there. They are also

having certain kind of you know characteristics requirements as well. So, those things we are going to discuss now.

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In addition to 3 main raw materials, a wide variety of other minerals, salt, oxides are also used as fluxing agents and special refractory ingredients. Fluxing agents, they purpose, they reduce the reaction temperature or vitrification temperature. That is the reason you need to have such fluxing agents.

And then, special refractory ingredients are required because these are infusible even at high temperatures of 1400 1500 degree centigrades, ok. They also provide some kind of vitrification to the product. Some fluxing agents that lower vitrification temperature or reaction temperature are provided here. Likewise, some common special refractory ingredients are provided here.

Many other raw materials are also used in various combinations as well. And then at least 450 have been classified as a kind of important raw material from different applications point of view. 450 out of which 3 are very much essential clay, feldspar and then sand or flint. So, that is about the raw materials and then their characteristics, importance, etcetera from the ceramic industry point of view.

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Chemical Conversions & Basic Ceramic Chemistry

- Ceramic products are prepared by combining different amounts of raw materials discussed, shaping and heating to firing temperatures
- Required temperatures may range
 - As low as 700°C (for over-glaze products)
 - As high as 2000°C (for many vitrified products)
- Firing at such range of temperatures leads to various reactions which are chemical bases for chemical conversions
- A few of important reactions include:
 - Dehydration or chemical water smoking at 150 – 650°C
 - Calcination, for e.g., calcination of CaCO_3 at 600 – 900°C
 - Oxidation of ferrous iron and organic matter at 350 – 900°C
 - Silicate formation at $\geq 900^\circ\text{C}$ * compare *

Now, we are going to see second important topic of the today's lecture that is basic ceramic chemistry. Chemical conversions and basic ceramic chemistry. Ceramic products are prepared by combining different amounts of raw materials that we have discussed, shaping and heating to firing temperatures.

Required temperatures may range, may range from several 100 degree centigrades to several 1000 degree centigrades as well as per the requirement. Let us say if you wanted to have a over glaze product, then required temperature may be as low as 700 degree centigrades only. But if you wanted to have many vitrified products as like glass products or you know, vitrified ceramic products, etcetera. So, the temperature would be as high as 2000 degree centigrades, ok.

Firing at such range of temperatures leads to various reactions which are chemical basis for chemical conversions, right. A few important reactions include dehydration or chemical water smoking at 150 to 650 degree centigrades. Then, calcination for example, calcination of calcium carbonate at 600 to 900 degree centigrades. And then, oxidation of ferrous iron and organic matter at 350 to 900 degree centigrades. And then, silicate formation beyond 900 degree centigrades.

Now, you see, these are the generalized reaction nature. Not only these reactions, there may be another number of reactions may also be possible. But categorically, if you

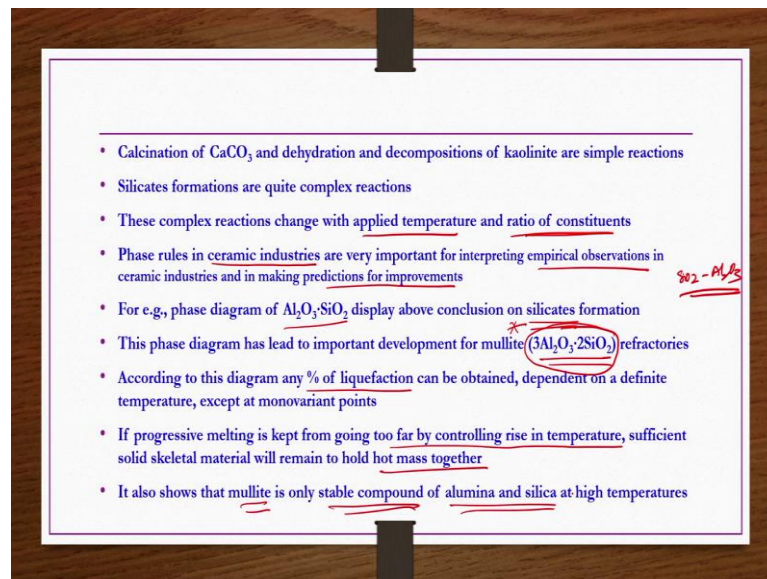
wanted to present, these are the 4 important reactions that are possible in basic ceramic industry when the ceramic product is produced.

Now, they are not like that individually step by step they take place, right. So, you can see here let us say at 600 degree centigrades, dehydration may also take place, calcination may also take place, and even oxidation of ferrous iron materials may also take place, right.

So, at a given temperature, more than one of these steps may possible. But however, at temperature more than 900 degree centigrade, only silicate formation takes place. Silicate formation taking place; that means, product formation is taking place, right. And then what you realize here, these reactions, whatever the dehydration, calcination, oxidation reactions are there, simple reactions, not much chemistry to understand.

But whatever this silicate formation taking place beyond 900 degree centigrade, they are very complex. Very complex reactions are there, very difficult to realize them, ok.

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So, calcination of calcium carbonate and dehydration and decomposition of kaolinite are very simple reactions. But silicates formations are quite complex reactions. These complex reactions obviously, change with the applied temperature and constituents of the raw materials that has been taken to prepare or to make a given ceramic product.

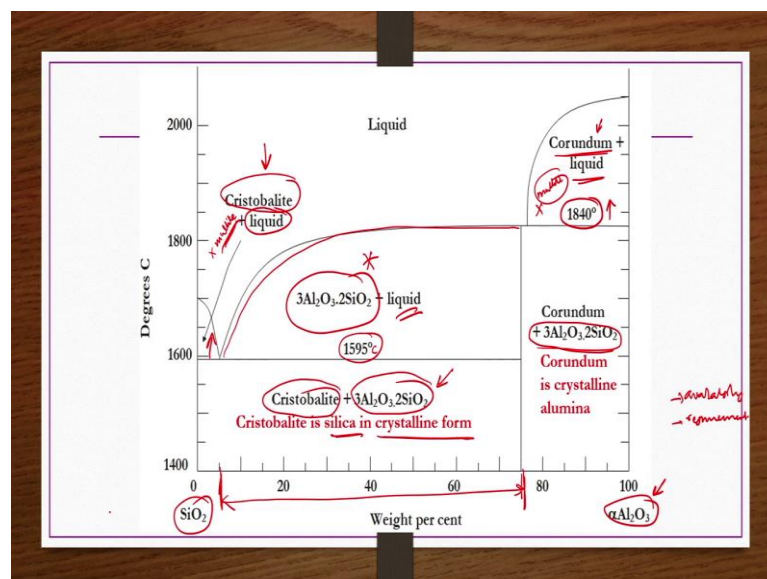
So, obviously, phase diagram or phase rule in ceramic industries are very important for interpreting empirical observations in ceramic industries and in making predictions for improvements. We are going to see a phase diagram of SiO₂, Al₂O₃. Then, you can realize how much important if you have the information of phase diagram for a given combination of material from the product point of view, ok. That we are going to see in the next slide.

For example, phase diagram of Al₂O₃, SiO₂ display above conclusion on silicate formation, that silicate formation is very complicated reaction. This phase diagram has led to important development of mullite refractories, right. Or the many of the refractories are mullite type refractories which are having 3Al₂O₃.2SiO₂ chemical formula, ok.

According to this phase diagram, any percentage of liquefaction can be obtained. If you have pure SiO₂ and then Al₂O₃, then it is a different thing. But if you have a combination of these two, any percent, 10 percent to 90 percent, so then you know you can obtain the liquefaction at lower temperature itself, right.

If progressive melting is kept from going too far by controlling rise in temperature, sufficient solid skeletal material will remain to hold hot mass together. It shows that mullite is only stable compound of alumina and silica at high temperatures that you see here in this slide, ok.

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So, now here, what we have a? We have a pure silica and then we have a pure alpha alumina. Now, if you have a pure silica, less than 10 percent alumina mixed with the silica, then you know what happens? Liquid and then cristobalite. Cristobalite is nothing but the crystalline silica. It is nothing but crystalline form of the silica is known as the cristobalite that you can get you know if you operate at the temperature more than 1595 degree centigrade, right.

And then, if you have almost like pure alumina, that is you know only less than 20 percent, 20, 25 percent of silica only present, then you can have a liquid sample plus corundum, which is nothing but crystalline alumina. This corundum is nothing but the crystalline alumina at temperatures more than 1840 degree centigrade, right.

But if you have any percentage of these two from you know let us say 10 to 75 percent, if you take 10 to 75 percent of alumina and silica and then apply the temperature, higher temperatures, what you can see? Irrespective of the composition, irrespective of the composition in this range, you get mullite. Along with that one, there would also be some cristobalite, which is nothing but crystalline silica. It is possible up to 1595 degree centigrades.

But however, if you do not want any crystalline silica, you need a liquid sample and then what you do? You further increase the temperature. So, within the same composition range, you can get still mullite you get and then liquids you get within this envelope. You can wear the composition variations are there between 10 to 75 percent of alumina and silica, right.

But now, here you can see if you have almost like pure alumina. So, then corundum and then mullite, here also you get mullite up to the temperature of 1840 degree centigrades. But if you go beyond this temperature, you do not get mullite here, right. Here also for the silica, which is almost pure silica with little alumina, then if you go beyond this temperature of 1595 degree centigrade, you get liquid as well as the cristobalite silica, right. But you do not get any mullite. Mullite has been found to be very good refractory.

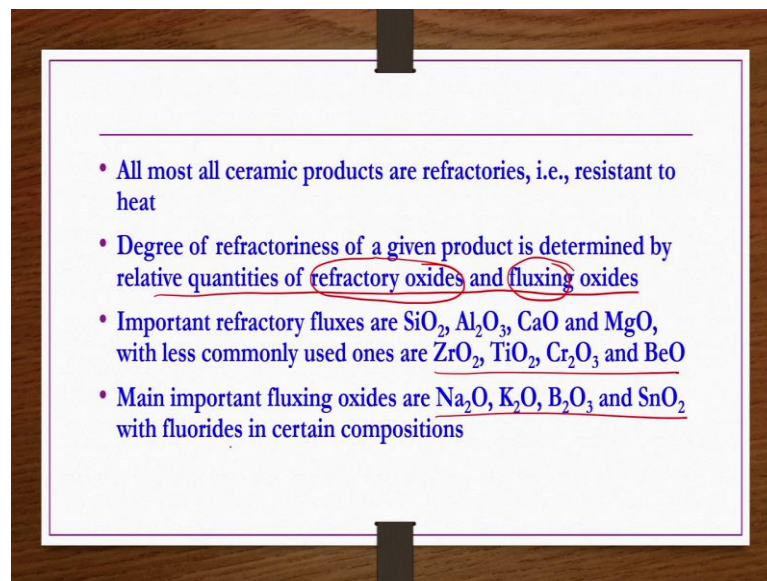
So, if you are targeting that one so; and then what is your source of SiO_2 and then Al_2O_3 . Accordingly, you take a composition and then you make a mixture, so then definitely you are going to get a mullite as long as the variation of the composition is

between 10 to 75 percent and in temperature, it is even at 1400 degree centigrades also, these formation are taking place.

So, now availability of these two components and then requirement of the products. What do you want to have in the products? You want to have more corundum in along with the mullite or you want to have more cristobalite along with the mullite in your final product at higher temperature. So, accordingly you can design the composition. Accordingly, you can design the temperatures, application temperature, ok.

So, now you can see how much essential to understand phase diagram. If you have a phase diagram. So, you can get so much information from the product point of view. Let us say mullite is one of the example here.

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Almost all ceramic products are refractories that is resistant to heat. Degree of refractoriness of a given product is determined by the relative quantities of refractory oxides and fluxing oxides. Fluxing oxides we have seen. So, fluxing oxides, they reduce the reaction temperature or vitrification temperature. Whereas, the refractory oxides, they provide required thermal resistance or thermal stability.

Important refractory fluxes are given here, but there are some less commonly used to fluxes, refractory fluxes are also there here, given here. Main important fluxing oxides are these things. With fluorides in certain compressions are also possible.

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- In all ceramic products, clay (such as kaolinite, mostly) is common ingredient
- Thus its reaction with applied high temperature are essential to understand
- At 600 - 650°C, the applied energy drives off the water of hydration
- At this temperature range, the much of the heat is also absorbed by constituents and leaving an amorphous mixture of alumina and silica
- $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 2 \text{SiO}_2 + 2 \text{H}_2\text{O}$
- These observations at this range of temperature are confirmed by x-ray studies
- A large portion of alumina can also be extracted with hydrochloric acid at this stage of applied temperature range

So, now what we understand until now, in ceramic products, clay such as kaolinite, mostly not the only one is very common ingredient. And then thus, its reaction with applied high temperature or essential to understand, right. So, at 600 to 650 degree centigrade, the applied energy drives off the water of hydration that is, you know dehydration reaction etcetera takes place.

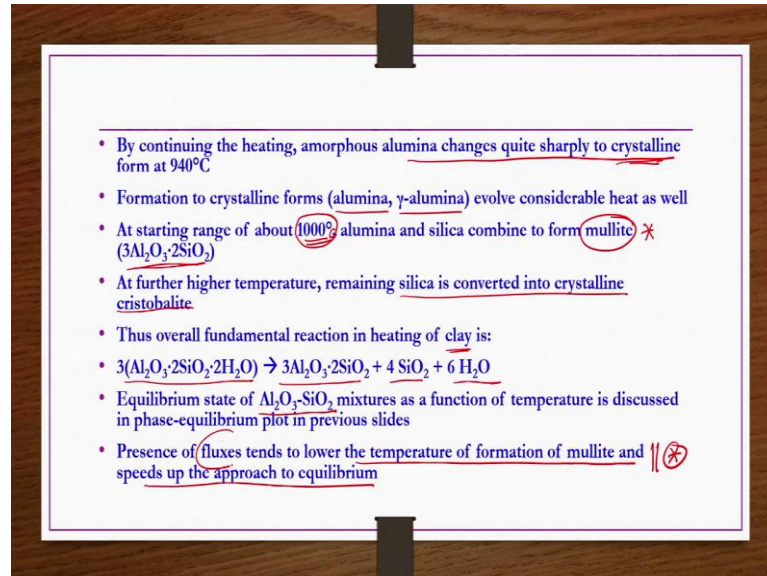
Further, at this temperature, what happens? Much of the heat is also absorbed by the constituents and leaving an amorphous mixture of alumina and silica as per the reaction. Let us say you have kaolinite and then supply the temperature of 600 to 650 degree centigrades, then you can get amorphous alumina, amorphous silica along with the water vapor.

So, not only the dehydration taking place, but also getting the amorphous constituents of the mixture. Individual components of the mixture you get in the amorphous form, that is alumina and silica you are getting in amorphous form, that is possible reaction. These observation at this range of temperature are confirmed by the x-ray studies. Actually, these are taking place in high temperature furnaces etcetera, all those, you know, refractories etcetera.

Then, how to realize what is happening, what components are forming etcetera. So, for those kind of solid state physics point of view, x-ray diffraction is one of the easily available tool to conform the product formation. What are the products are being

formed? Ok. A large portion of alumina can also be extracted with hydrochloric acid at this stage of applied temperature range as well.

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Now, what happens if you keep on increasing the temperature? Right. By continuing the heating, amorphous alumina changes quite sharply to crystalline form at 940 degree centigrade by forming corundum. Corundum is nothing but crystalline alumina. Formation to crystalline forms of alumina or gamma alumina evolve considerable heat as well. So, at starting range of 1000 degree centigrades, you are gradually increasing temperature. So, 600 to 650 degree centigrade, what happens?

Mostly dehydration takes place plus formation of the amorphous alumina and silica formation may also take place as per the phase diagram, those things we have seen. But if you further increase the temperature to 940 degree centigrades, etcetera, what you are getting?

You are getting in a crystalline form of alumina. If you further increase the temperature to 1000 degree centigrades, what happened? Alumina and silica combine to form mullite, ok. So, this is very essential. This is the one of the base refractory that is available.

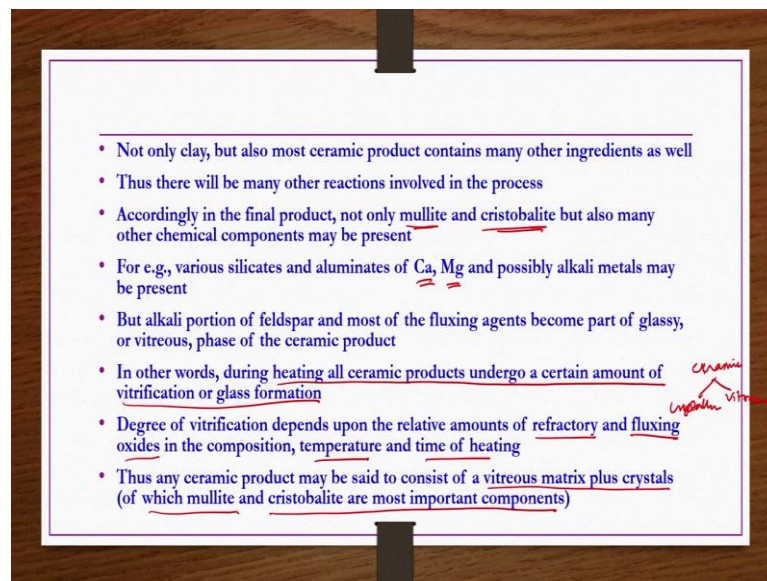
At further higher temperature, remaining silica is converted into crystalline cristobalite. Cristobalite is nothing, but crystalline silica. So, thus overall fundamental reaction in

heating of clay is this one. Like kaolinite, 3 moles of kaolinite, if you react, you get 3 moles of mullite and then 4 moles of silica and 6 moles of water vapor, ok.

Equilibrium state of alumina and silica mixtures as function of temperature is discussed in phase diagram anyway. Presence of fluxes tends to lower the temperature of formation of mullite and speeds up the approach to equilibrium. So, that is the importance of this fluxing agents, ok.

Now, we have seen that 3 are main important raw materials, clay, feldspar and sand as a flint, etcetera, right. So, but we also realize there are many other raw materials or also there, they may be in minor quantities. So, obviously, not only the reaction that we have discussed in the previous slide, many other reactions may also possible, ok.

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Not only clay, but also more ceramic product contains many other ingredients as well. So, thus there will be many other reactions involved in the process. And accordingly, in the final product, not only mullite, cristobalite, but also many other chemical components may also be present, obviously. For example, various silicates and the aluminates of calcium, magnesium and possibly, alkali metals may also be present in the final product, ok.

But alkali portion of feldspar and most of the fluxing agents become part of glassy or vitreous phase of the ceramic product, ok. In other words, during heating all ceramic

products undergo a certain amount of vitrification or glass formation. So, what do you understand? Ceramic products you can see now as a kind of some kind of crystalline material plus some kind of vitreous nature, ok.

So, thus degree of vitrification depends upon the relative amounts of refractory and then fluxing oxides in the composition and then temperature and time of heating. Thus, any ceramic product may be said to consist of a vitreous matrix plus crystals of which mullite and cristobalite are most important components, ok.

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• Below given common classification of ceramic products is based on degree of vitrification or progressive reduction in porosity

Type of ceramics	Range of fluxing agents	Heating range	Degree of vitrification
Whitewares	Varying amounts	Moderately high temperature	Varying vitrification
Heavy-clay products	Abundant	Low temperature	Little vitrification
Refractories	Few fluxes	High temperatures	Little vitrification
Enamels	Very abundant fluxes	Moderate temperature	Complete vitrification
Glass	Moderate flux	High temperatures	Complete vitrification

Now, we have already realized that any ceramic product may be said as a kind of vitreous matrix with crystals. So, now based on the degree of vitrification, we try to do a classification, right. Then, what we have? Whitewares, heavy-clay products, refractories, enamels, glass we are taking and the types of ceramics. Then, what are the corresponding fluxing agents? Heating range and degree of vitrification we have here.

If you have whitewares, so then fluxing agents, range varying amounts have and then heating range may be moderately high temperature. So, varying degree of vitrification is possible because varying amounts of fluxing agents you are taking and then also the applied temperature is moderately high temperature.

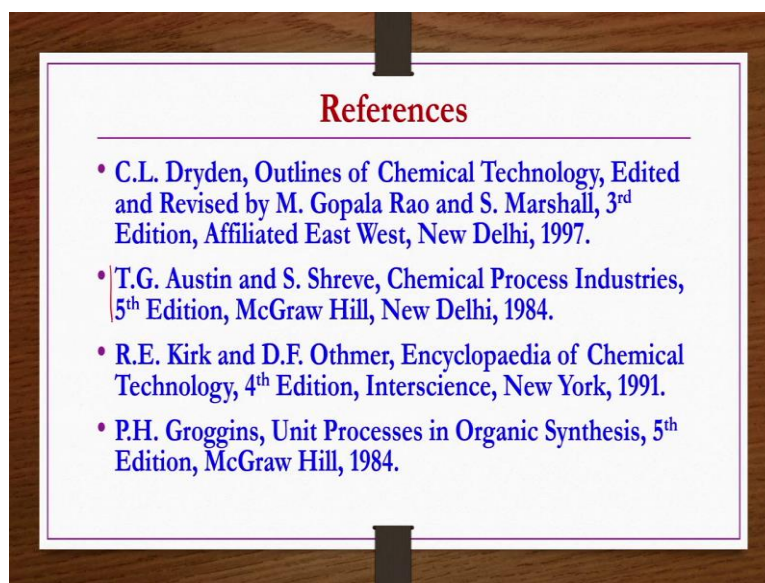
Whereas in heavy clay products, fluxing agents are present in abundant, but despite of that one, vitrification is not high, it is only little that is because the applied temperature is

low. Vitrification takes place better at high temperatures, ok. So, though here fluxing agents you are having abundant, but the applied temperature is low. So, that is the reason you are getting little vitrification.

Then refractories, few fluxes are there and then high temperatures are the range of heating. So, since the fluxes are few, you have the little vitrification here as well. Enamels, very abundant flux and then moderately high temperatures are there. So, then obviously, complete vitrification is possible. Glasses, moderate flux, but the temperatures are very high.

If you have high temperature or high heating range with whatever the moderate fluxing agents, you can get complete vitrification. So, that we have already seen in the glass industry anyway. So, this is all about basic raw materials and then basic ceramic chemistry, right. References for this particular lecture are provided here.

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But however, the entire lecture is prepared from this reference book.

Thank you.